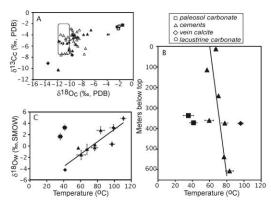
## Stable and Clumped Isotope Analysis of Eocene Fenghuo Shan Group Sediments: Implications for Paleoelevation Estimates and Carbonate Diagenesis

Kathryn E. Snell<sup>1</sup>, Peter C. Lippert<sup>1</sup>, John M. Eiler<sup>2</sup>

The uplift history of the Tibetan Plateau is currently a subject of debate. Models of plateau growth vary in time, from pre-India-Asia collision (e.g., 100 Ma ago) to gradual uplift after the India-Asia collision (e.g., 55 Ma ago), to more recent abrupt uplift (<7 Ma ago). Models of plateau growth also vary in space, from northward stepwise growth of topography to simultaneous surface uplift across the plateau. Oxygen isotope paleoaltimetry studies have been used to estimate the elevation of the plateau in the past, but this technique requires assumptions about the temperature of mineral formation. Independent estimates of the temperature of mineral formation, available from the carbonate clumped-isotope ( $\Delta_{47}$ ) thermometer (Ghosh and others, 2006), may identify post-depositional recrystallization and/or isotopic exchange in carbonate samples. When plausible primary depositional temperatures are found, the  $\Delta_{47}$  temperature estimates and the calcite  $\delta^{18}$ O ( $\delta^{18}$ O<sub>c</sub>) can be used to make more accurate estimates of  $\delta^{18}$ O of the waters ( $\delta^{18}$ O<sub>w</sub>) from which the calcite precipitated, assuming that the carbonates formed in equilibrium with clumped isotopes at the time of formation. This appears to be a reasonable approach for lacustrine carbonates and most soil carbonates, although some soil carbonates show disequilibrium effects that may be the result of rapid CO<sub>2</sub> degassing (Eiler and others, 2008).

Here we present preliminary clumped isotope ( $\Delta_{47}$ ) temperatures, calcite  $\delta^{13}C$  and  $\delta^{18}O$  ( $\delta^{13}C_c$  and  $\delta^{18}O_c$ ), and reconstructed water  $\delta^{18}O$  ( $\delta^{18}O_w$ ) values from paleosol carbonates and calcite cemented siliciclastic sediments of the early Eocene-aged Fenghuo Shan Group (FHSG). We collected samples from the TouTou He subbasin of the Hoh Xil Basin on the central Tibetan Plateau. This section contains fluvial deposits that comprise cross-bedded sandstones, muddy rip-up conglomerates and overbank successions with some incipient paleosol development. We collected paleosol carbonates from a limited number of horizons and carbonate-cemented siltstones and mudstones throughout the section. Both the paleosol carbonates and carbonate-cemented siliciclastic rocks contain additional secondary carbonates, typically in the form of vein-filling calcite. Lastly, for comparison with previous stable isotope studies on FHSG sediments (Cyr and others, 2006), we collected one lacustrine carbonate from a separate, nearby outcrop of FHSG deposits.



**Figure 1.** A: Plot of  $\delta^{13}C_c$  versus  $\delta^{18}O_c$ . Filled symbols represent the subset of samples used for  $\Delta_{47}$  analyses. Rectangle represents the range of  $\delta^{13}C_c$  and  $\delta^{18}O_c$  of the lacustrine carbonates from Cyr et al., 2005. B: stratigraphic level versus  $\Delta_{47}$  temperature. C:  $\delta^{18}O_w$  versus  $\Delta_{47}$  temperature. Error bars shown represent  $1\sigma$  standard errors. Data points without visible error bars have errors that are smaller than the size of the symbol.

 $\delta^{13}C_c$  and  $\delta^{18}O_c$  values for the secondary carbonates (cements and vein calcite) range from -3 to -10 ‰ (PDB) and -7 to -14 ‰ (PDB), respectively (Figure 1A). The limestone  $\delta^{13}C_c$  and  $\delta^{18}O_c$  values are similar to the secondary carbonate samples, and to the previously published  $\delta^{13}C_c$  and  $\delta^{18}O_c$  values from Fenghuo Shan Group lacustrine carbonates. The paleosol carbonates plot separately from these samples, and their  $\delta^{13}C_c$  and  $\delta^{18}O_c$  values range from -2 to -4 ‰ (PDB) and -1.6 to -4 ‰ (PDB), respectively. The  $\Delta_{47}$  temperature estimates for a subset of the cements range from 57-83°C, and decrease up-section at a gradient of 30°C/km (Figure 1B). The vein calcite  $\Delta_{47}$  temperature estimates range from 96 to 100°C.

<sup>&</sup>lt;sup>1</sup> Earth and Planetary Sciences Department, University of California Santa Cruz, Santa Cruz, CA 95060, U.S.A., ksnell@pmc.ucsc.edu

<sup>&</sup>lt;sup>2</sup> Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, 91125, U.S.A.

These temperatures are all too high to represent earth-surface temperatures but are reasonable burial temperatures given estimates of the burial history of the region. The total thickness of Cenozoic basin sediments in this area are estimated to be between 3-5 km, with our section composing the base of this succession (Liu and Wang, 2001; Coward and others, 1988). Vitrinite reflectance data (personal communication, Haisheng Yi, CITS, Chengdu) from the overlying Yaxicuo Group suggest FHSG sediments have been exposed to maximum burial temperatures of up to 180°C, depending on actual thicknesses of the FHSG. Interestingly, the  $\Delta_{47}$  temperature estimate from our limestone sample (111°C) is also too hot to represent the original depositional temperature. Rather, it appears to be reset to burial temperatures. This is consistent with the presence of significantly thermally altered organic biomarkers in these lacustrine carbonates (Polissar and others, 2009). Finally, the  $\delta^{18}O_w$  values calculated for these samples range from -4 to 5% (SMOW), and change linearly with temperature by  $\sim 0.1\%$ °C (Figure 1C).

Collectively, these data challenge the original assumption that because the primary (ie. lacustrine carbonate) and secondary carbonates had similar  $\delta^{13}C_c$  and  $\delta^{18}O_c$  values, the secondary carbonates precipitated from similar shallow, low-temperature waters as the lacustrine carbonates. Rather, these data suggest that, at minimum, diagenetic alteration reordered the isotopes within our lacustrine carbonate sample. Alteration under closed-system conditions could preserve the original bulk  $\delta^{13}C_c$  and  $\delta^{18}O_c$  values. Given the evidence for diagenetic isotopic reordering, however, the extent of alteration and possibility for open-system isotopic exchange should be re-evaluated for the FHSG lacustrine carbonates.

Although the lacustrine carbonates reflect isotopic reordering, the paleosol carbonates may preserve their primary isotopic signature. The distinction of their  $\delta^{13}C_c$  and  $\delta^{18}O_c$  values from the secondary carbonates and their lower  $\Delta_{47}$  temperature estimates (35°C and 41°C) suggest, at minimum, that if these samples have been diagenetically altered, they have not been altered to the same extent as the lacustrine carbonates. These temperatures are warm for earth-surface temperatures, but are plausible considering that soil carbonate formation may be biased towards the summer months, and that soil temperatures can be increased with respect to surface air temperatures due to radiative heating. Additionally, as these sections were likely ~10° farther south than they are at present (Lippert and others, 2009), and were deposited during the early Eocene, the warmest time of the Cenozoic, the high calculated temperatures of the paleosol carbonates could possibly be the original formation temperatures. If these are primary temperatures, then the relatively <sup>18</sup>O-enriched signature of the soil water (>1 %) may reflect highly evaporated soil waters, implying relatively dry conditions. Because of the potential that the  $\delta^{18}O_w$  has been affected by evaporation, and the limited number of primary temperature calculations, paleoelevation estimates based on this current dataset are extremely speculative. However, the relatively high temperatures and fairly <sup>18</sup>O-enriched soil water values are more consistent with a low elevation site than high elevations, suggesting that this region was uplifted to its current elevation later than ~40 Ma.

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